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Multiscale modelling of materials chemomechanics: brittle fracture of oxides and semiconductors

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Abstract

Fracture is one of the most challenging ‘multi-scale’ problems to model: since crack propagation is driven by the concentration of a long-range stress field at an atomically sharp crack tip, an accurate description of the chemical processes occurring in the small crack tip region is therefore essential, as is the inclusion of a much larger region in the model systems. Both these requirements can be met by combining a quantum mechanical description of the crack tip with a classical atomistic model that captures the long-range elastic behaviour of the surrounding crystal matrix. Examples of the application of these techniques to fracture problems include: low-speed dynamical fracture instabilities in silicon; interactions between moving cracks and material defects such as dislocations or impurities; the crossover from thermally activated to catastrophic fracture; very slow crack propagation via kink formation and migration; and chemically activated fracture, where cracks advance under the concerted action of stress and corrosion by chemical species such as oxygen or water.

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1. Introduction

Fracture is the main lifetime limiting failure mode of many materials, from metals to ceramics and glasses, and is typically divided into two broad classes: brittle and ductile. In brittle fracture, there is no plastic deformation, and failure occurs along particular low-energy cleavage planes. In contrast, ductile materials such as steel tend to fail with a large amount of plastic deformation (necking), pulling apart to leave rough fracture surfaces. The same patterns are evident upon closer examination: brittle cracks are found to be atomically sharp, proceeding bond by bond, while ductile cracks remain rough at the microscale, driven by the formation and coalescence of microscopic voids.

Fracture of oxides and semiconductors is of tremendous technological relevance. For example, fracture of silicates is relevant both to mining, where huge amounts of energy are required to fragment thousands of tons of rock into fine powder — around 5% of total human energy consumption, according to a recent review by the World Business

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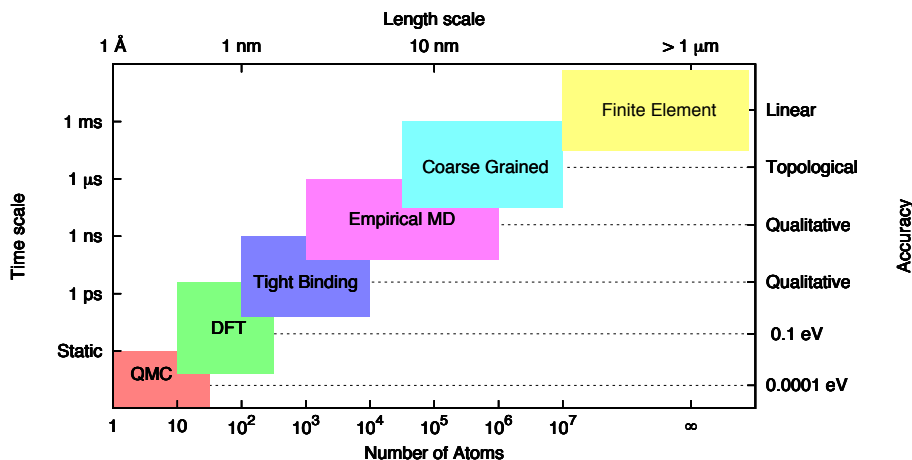


Fig. 1: Schematic representation of the range of length- and time-scales accessible to a variety of modelling methods, from quantum Monte Carlo (QMC) for very accurate, very expensive static calculations through to more approximate methods such as finite-element modelling.

Council for Sustainable Development (2009) — and to modern ceramic prostheses, such as dental implants made of silica-rich porcelain, which have to survive years of tough mechanical work in the wet environment of the human body without breaking (Chevalier, 2006).

These seemingly very different processes share a remarkably similar underlying chemistry, with cracking driven by ‘chemomechanical’ processes where stress fields and chemistry are tightly coupled. This is particularly evident for stress corrosion cracking (SCC) of oxides, where a chemically aggressive environment which can cause cracks to form very slowly at unexpectedly low mechanical loads. In spite of its fundamental scientific interest and great importance for applications, the way oxide materials break at the atomic scale is almost completely unknown, with the result that the control of crack propagation, albeit highly desirable, is very difficult to achieve (Kermode et al., 2011; Jaeger et al., 2007). Owing to the universal nature of many aspects of crack growth, such as the magnification of the applied stress at a crack tip, fracture in any ceramic in a water-rich environment is expected to be rather similar so there is much to be learnt from simulations in model systems (Lawn, 1993).

2. Multiscale Modelling Approach

The study of fracture mechanics dates back around 100 years, to Griffith (1921), who first proposed a thermodynamic energy balance criteria to understand and predict when cracks will propagate. His key idea was that stress concentrates at pre-existing flaws: this was motivated by the observation that materials break at much lower loads than the theoretical stress needed to break their chemical bonds. This analysis leads to a critical flow of energy to a crack tip, or energy release rate, $G_c = 2\gamma$, where γ is the surface energy density. Crack advance becomes energetically favourable when the energy flow to the crack tip exceeds the cost of creating two new surfaces, i.e. for $G > G_c$.

Much further work has been carried out to understand fracture at the continuum level (Freund, 1998; Lawn, 1993), but here our goal here is to simulate fracture at the atomic level, to examine the combined effects of stress and chemistry (Marder, 2004). A hierarchy of materials modelling techniques have been developed in recent decades, as illustrated in Fig. 1. A first approach to atomic-scale fracture modelling would be to use classical interatomic potentials to carry out molecular dynamics (MD), since this technique can be used for systems containing millions of atoms and up to microsecond timescales, which are both adequate in principle to describe the strain gradients and crack speeds encountered in typical fracture processes. However, most classical interatomic potentials fail to accurately reproduce brittle fracture. This point can be illustrated by considering silicon, which has been much studied both experimentally and theoretically as a prototypical ideal brittle material. Below its brittle to ductile transition (BDT) temperature of around 500°C, silicon cleaves to leave atomically smooth fracture surfaces (Lawn, 1993). At higher temperatures,

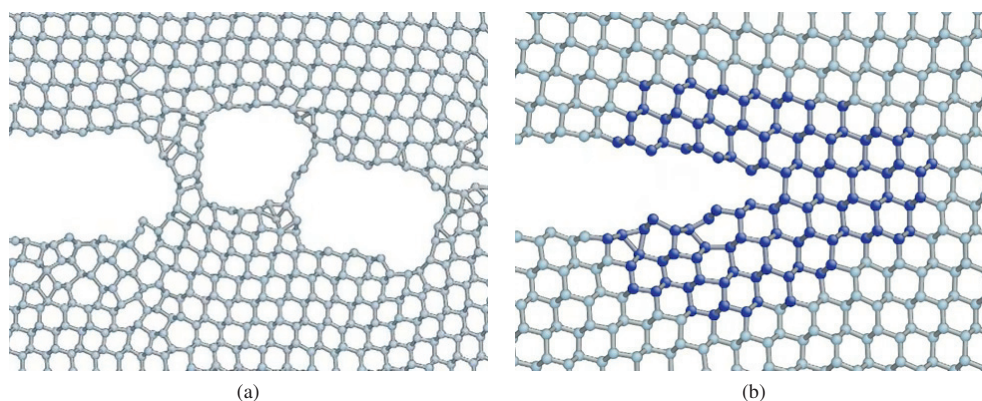


Fig. 2: Snapshots from MD simulations of fracture of silicon on the (111) cleavage plane with (a) the Stillinger and Weber (1985) classical interatomic potential; (b) the ‘Learn on the Fly’ (LOTF) scheme, with dark blue atoms treated at the quantum mechanical level (here, DFT) and gray atoms with the same classical potential as in panel (a). The classical simulation is unphysically ductile, while the LOTF simulation recovers the brittle material response, as well as correctly capturing chemical details such as the Pandey (1981) 2×1 reconstruction of the (111) surface.

fracture is ductile, with the emission of multiple dislocations from the tip. Fig. 2a illustrates how the Stillinger and Weber (1985) interatomic potential, which provides an otherwise excellent description of many properties of silicon, predicts a ductile material response for silicon in room temperature simulations well below the BDT, in contrast to the atomically smooth fracture surface observed in many experiments under the same conditions. This discrepancy is essentially due to stress concentration which has been shown to diverge as $\sigma \sim 1/\sqrt{r}$ near a crack tip (Irwin, 1948), leading to anharmonic stretching and rupture of bonds, which is typically not well captured by simple interatomic potentials (Bernstein and Hess, 2003; Buehler, 2008).

Most potentials overestimate the lattice trapping barrier Thomson et al. (1971), the energy barrier to bond breaking at a crack tip that arises from the periodicity of the crystalline lattice (in contrast to continuum methods where the crack tip advances continuously). This means that when fracture eventually does occur, there is too much energy available, which is then dissipated by a variety of plasticity mechanisms such as dislocation emission (cf. Fig. 2a). This leads to results in contrast with the expected brittle behaviour. Interestingly, however, continuum theories and simple potentials agree with one another until surprisingly close to the crack tip (~ 1 nanometre), where non-linear effects become important (Singh et al., 2014). The region where atomistic and continuum theories disagree is the non-linear process zone, where chemically interesting things are happening. In our hybrid multiscale approach, we treat this region at the quantum mechanical (QM) level.

Returning to Fig. 1, we note that QM approaches such as density functional theory (DFT) would correctly describe bond-breaking in silicon. However, the strong bidirectional coupling between bond-breaking at the crack tip and the long-range stress field driving fracture necessitates a multiscale approach. The reason a fully DFT approach is not practical is that the boundaries of the model system must be placed far enough away from the crack tip not to affect the results, which means that large cells containing tens- to hundreds- of thousands of atoms are needed. This exceeds the current capabilities of most QM approaches, and the applicability of traditional $O(N^3)$ -scaling DFT calculations to these problems has thus mostly been limited to small model systems (Perez and Gumbsch, 2000; Zhu et al., 2005).

The combined requirement of accuracy and efficiency can be met simultaneously with a hybrid QM/MM (quantum mechanical/molecular mechanical) scheme, where QM precision is used *only* where it is needed. The ‘Learn on the fly’ (LOTF) scheme (De Vita and Car, 1998; Csányi et al., 2004) provides one such non-uniform approach through which all atoms that are not suitably described by the classical potential used for the MM scheme are treated quantum-mechanically, by embedding a dynamically adjustable quantum mechanical region centred on the crack tip within a much larger classical system (Fig. 3). For the example of Fig. 2b, these atoms are those in the vicinity of the crack tip (coloured dark blue), where highly strained Si-Si bonds are present, and where formation and rupture of chemical bonds occurs during crack propagation.

Standard QM/MM techniques, usually developed for biological systems, typically adopt energy-based approaches (Warshel and Levitt, 1976). The total energy of the system is written as a combination of the QM energy, the MM

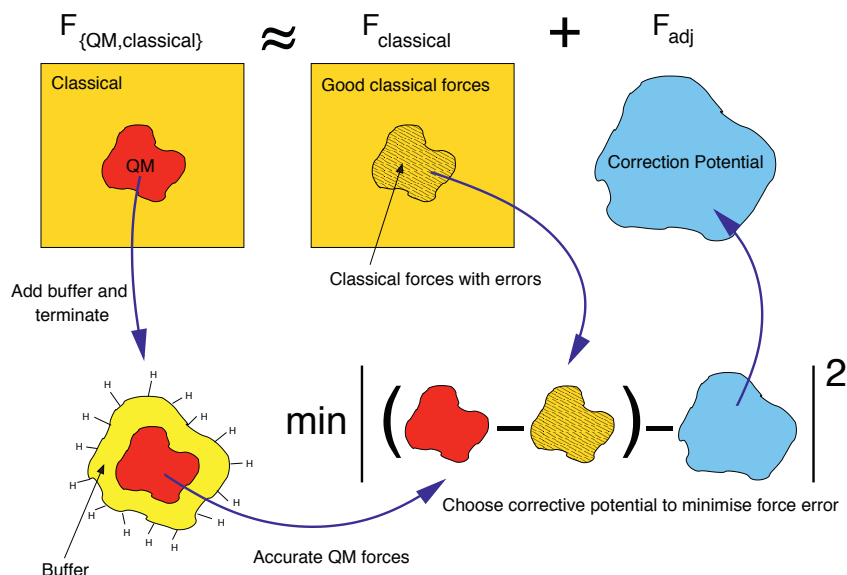


Fig. 3: Overview of the LOTF hybrid simulation method, which allows quantum mechanical accuracy to be embedded within a large molecular mechanical system, dynamically coupling DFT (red region) and empirical molecular dynamics (MM, yellow region). QM forces are evaluated using a cluster surrounded by a finite buffer and passivated with hydrogen atoms (lower left). A universal corrective potential (blue) is fit to the difference in QM and MM forces (lower right), and then the sum of the MM and corrective forces are used to advance the dynamics for several timesteps while the parameter remain valid. See text and references given there for more details.

energy and a QM/MM term, often specifically devised for a particular system, that takes care of the interaction between the two regions Svensson et al. (1996). While this approach allows the definition of a total energy which is conserved during the dynamics, the forces used to propagate the MD are not accurate enough because of the spurious effects due to the presence of the boundary between the QM and the MM regions Bernstein et al. (2009). Moreover, the necessity to suitably ‘terminate’ the QM region does not allow the QM region to move during the simulation, which is, however, required if we want to track the motion of a crack tip. The LOTF scheme instead adopts a force-based scheme, which allows the QM region to move during the MD simulation and accurate forces to be calculated even at the boundaries of the two regions. The full details of the scheme have been thoroughly presented in a number of articles (De Vita and Car, 1998; Csányi et al., 2004, 2005; Moras et al., 2010a; Kermode et al., 2008; Bernstein et al., 2009).

Modelling the crack tip region at the QM level in this way reproduces the expected brittle behaviour of silicon, as illustrated in Fig. 2(b). For the case of silicon, the fracture initiates at a much reduced energy release rate, and is much more brittle, with none of the artificial plasticity seen with the classical potential alone. The DFT model also gives an improved description of the fracture surfaces, which can be seen to reconstruct to form a Pandey (1981) π -bonded chain, with its characteristic alternating pentagons and heptagons. The approach also allows arbitrary complexity to be introduced in the crack-tip region without the need for reparameterisation of interatomic potentials, facilitating accurate simulations of chemomechanical processes. A further advantage of the scheme is that a predictor-corrector approach can be used to avoid the computational cost of carrying out QM calculations at every timestep. Typically this accelerates simulations by around a factor of ten, and there is considerable scope for further improvements in this factor by combining it with a Machine Learning (ML) approach which predicts QM forces from a database whenever possible, rather than calculating them, thus reducing the need for new QM calculations to the strict minimum (Li et al., 2014).

3. Discussion and Outlook

Due to the combined advances of algorithms and computing platforms, and the exquisite size- and time-resolution of the current generation of nanoscale experimental techniques (cf. e.g., Ciccotti et al. 2008 and Sherman et al. 2008),

there has never been a more propitious time for computational chemomechanics research projects. Indeed, early applications of the LOTF approach to fracture mostly concerned dynamic phenomena, but only recently have started to involve increasing crack tip chemistry. The LOTF method has been successfully used to investigate dynamical instabilities in silicon fracture (Kermode et al., 2008; Fernandez-Torre et al., 2010) the interactions between moving cracks and dislocations (Makov et al., 2009), as well as the first chemically-induced dynamical crack deflection/energy dissipation model for atomic impurities (Kermode et al., 2013b). LOTF applications to stress corrosion in Si involving hydrogen and oxygen reveal that molecules located near the crack tip can play the role of a corrosive agent, undergoing barrierless dissociation followed by chemisorption, and catalysing the rupture of highly stressed crack tip bonds. In particular, we find that hydrogen gas formation inside Si platelets (Moras et al., 2010b) or oxygen gas supply at accessible crack tips can cause sub-critical crack advance in silicon (Gleizer et al., 2013).

With the increased availability of increased high performance computing (HPC) capabilities, three-dimensional crack front effects such as slow propagation of cracks by the formation and advance of kinks are for the first time coming within reach. At the same time, prospects for applying the LOTF scheme to ductile metals are also good: projects are underway to study hydrogen embrittlement of steels and the mechanical properties of nickel-based super-alloys, a class of materials that exhibit excellent strength and creep-resistance at high temperatures, even in chemically aggressive environments, e.g. making them suitable for the construction of efficient turbines for energy generation and aerospace applications.

Returning to brittle materials, the nanoscale mechanism for subcritical “stress corrosion cracking” (SCC) has spurred considerable recent debate (Ciccotti, 2009). While chemomechanical processes involving stress, thermal activation and diffusion must contribute, it is not known which mechanisms dominate. The exact role water plays in crack propagation is also not yet fully understood. The LOTF scheme has very recently been extended to oxide systems, incorporating a novel linear-scaling polarisable interatomic potential for the classical region (Kermode et al., 2010), making the study of these technologically relevant problems feasible for the first time. The role of chemomechanical processes in silica fracture forms the subject of an extensive ongoing investigation, powered by Leadership-class HPC resources at Argonne National Laboratory provided by the US DoE under the INCITE programme (Kermode et al., 2013a).

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